

ACID-BASE INTERACTIONS OF NICOTINE AND PYRIDINE ON SURFACES

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ABSTRACT

Two different experimental approaches were employed to gain insight into the molecular interactions of nicotine and pyridine with simple and well-characterized materials. We investigated nicotine desorption from Teflon and cotton surfaces in a flow chamber experiment and developed an ATR-FTIR spectrophotometric method to study the molecular association of pyridine with materials representative of certain indoor surfaces (cellulose and gypsum). The experimental results suggest the presence of two sorptive states for volatile amines. Spectroscopic evidence for acid-base interactions with surfaces is consistent with the observed desorption behavior.

INDEX TERMS

Acid-base, nicotine, pyridine, sorption, surface materials.

INTRODUCTION

The extent to which volatile and semivolatile organic chemicals adhere and remain associated with indoor materials varies widely, depending on their vapor pressure and molecular interactions with surface sites (Goss 1997; Singer et al 2004). We hypothesize that the ability to associate through acid-base processes is critical to understanding the indoor dynamics of volatile amines that are present in tobacco smoke and other indoor pollution sources. Webb et al. (2002) found that NH_3 (g) increased nicotine desorption, and inferred that this observation was related to the influence of acid-base reactions on the sorption process. The goal of this work is to explore fundamental aspects of the interplay between acid-base surface chemistry and sorption of volatile and semivolatile alkaline chemicals on model materials. We selected simple surfaces that are representative of various chemical functionalities and that exhibit different water uptake capacities.

EXPERIMENTAL

Chamber Experiments: We performed a series of experiments to quantify nicotine sorptive partitioning and desorption rates for a matrix of two experimental variables: surface material (Teflon or cotton cloth) and humidity level (dry air or 65-70 % RH). A 200-L reaction chamber was constructed from gypsum wallboard panels covered with a Teflon bench protector film, the only internally exposed material. Clean air and nicotine vapor were introduced via two inlet ports located on opposite corners. Clean air was

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supplied at 5 L min^{-1} ($\pm <1\%$), for an air change rate of 1.5 h^{-1} . In experiments employing humidified air, the flow was directed through a bubbler filled with deionized water. Nicotine vapor was provided by passing air at 5 L min^{-1} through a glass tube housing a diffusion vessel loaded with liquid nicotine; the tube was maintained at 22°C in a water bath. Air exited the chamber through a single port, located at the center of the top panel. Nicotine samples were collected at a stainless steel tee just above the outlet port using Tenax-TA sorbent tubes. Temperature ($21.5 - 22.5^\circ\text{C}$) and RH were monitored continuously in an auxiliary chamber into which the main chamber exhaust was directed. Sorbent tubes were analyzed by thermal desorption gas chromatography (TD/GC) employing either nitrogen-phosphorus (NPD) or mass selective detection (MSD).

The cotton cloth employed in this study was uncolored, untreated, and preconditioned only by washing with hot water and machine drying. Rectangular pieces each measuring $28.2 \times 75.5 \text{ cm}$ were attached to two internal walls, positioned symmetrically with respect to both inlets and the outlet. Partial coverage of chamber surfaces was sufficient owing to the much higher sorption capacity of cotton. Following chamber conditioning at the desired RH, adsorption was initiated by connecting the nicotine flow to the chamber. The chamber was operated as described for a period of 12 to 24 h to reach sorptive equilibrium at nicotine gas-phase concentrations of 1-2 ppm (12-14 ng/mL). The desorption phase was initiated by disconnecting the nicotine source from the chamber. Samples were collected at intervals consistent with the nicotine concentration change during one week.

ATR-FTIR Experiments: Interactions between the sorbate and the surface were further explored with surface spectroscopy to gain insight into the molecular nature of the sorption process. Fourier transform infrared (FTIR) spectra of pyridine sorbed on gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and cellulose were collected on an attenuated total reflection (ATR) crystal, as described by Sayer and Horn (2003). Fine powders ($< 100\text{-}125$ mesh) of each sorbent material were suspended in a solution of 10% pyridine in acetonitrile. The slurries were applied over the surface of a ZnSe ATR crystal (4.06 cm^2) inside the FTIR spectrophotometer. The infrared beam incidence angle (40°) determined an effective penetration depth of $0.5\text{-}1.0 \mu\text{m}$ into the sample for the studied wavelength range. A gentle N_2 stream was applied over the surface of the ATR crystal to accelerate evaporation of the acetonitrile solvent, as monitored by the disappearance of the $\text{C}\equiv\text{N}$ stretching band at 2220 cm^{-1} . The N_2 atmosphere also prevented the uptake of moisture from surrounding air. Once the evaporation of acetonitrile was complete, spectra in the range $400\text{-}4000 \text{ cm}^{-1}$ were recorded at ~ 2 -minute intervals until pyridine was substantially desorbed (22 min for cellulose, 55 min for gypsum). Gravimetric measurements after each experiment indicated 19-36 mg dry sorbent material deposited, corresponding to film thickness between 20 and $38 \mu\text{m}$.

RESULTS AND DISCUSSION

Chamber Experiments: Figure 1 shows the desorption dynamics of nicotine from Teflon (Fig 1-A) and cotton cloth (Fig 1-B) under a constant flow of dry air corresponding to an air change rate of 1.5 h^{-1} . In both experiments the gas-phase concentrations initially decreased at approximately the ventilation removal rate (solid gray line). For Teflon, this non-sorptive decay phase lasted for $\sim 5 \text{ h}$, corresponding to a 99% (2 order of magnitude)

reduction in gas-phase concentration. Relatively higher desorption mass transfer from cotton resulted in an earlier deviation from exponential decay with ventilation; the profile departed from ideal non-sorptive behavior when concentrations were still >10% of initial levels. In both cases the shape of the long-term ($t > 5$ h) profile was determined by the magnitude and rate of desorption. Mid-week concentrations were 3 orders of magnitude below initial levels for the Teflon-only experiment (i.e. at 1-2 ppb) and 2 orders of magnitude below initial levels for cotton.

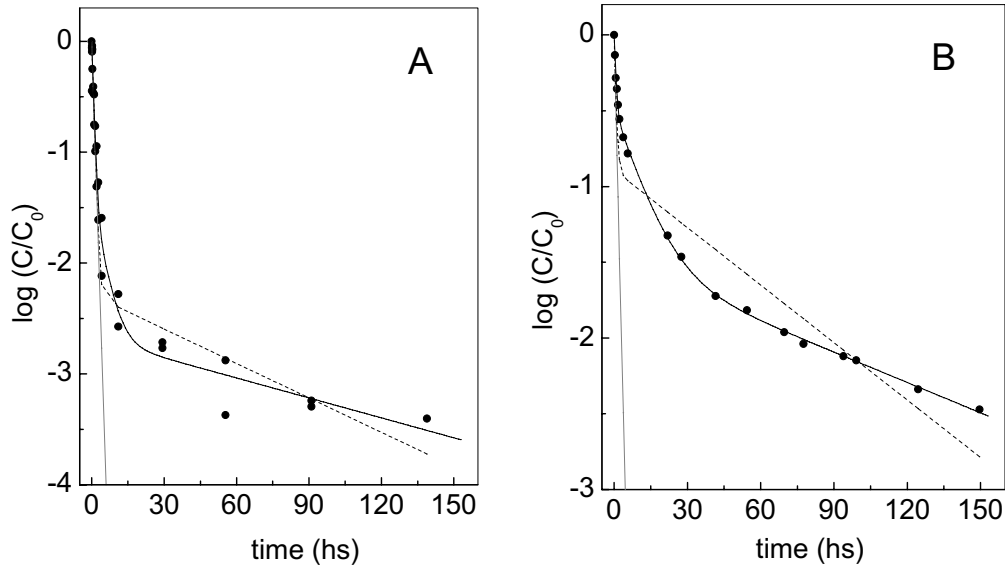


Figure 1: desorption of nicotine from (A) Teflon surfaces, and (B) a cotton cloth. Experimental data (●) are shown with curves corresponding to 1-sink model (---), 2-sink model (—) and non-sorptive ideal behavior (—).

Experiments performed with humid air (RH = 65-70 %) yielded similar results, particularly for Teflon surfaces. Notably, the desorption curve of cotton was not affected dramatically by the presence of water, despite its large water uptake. We performed additional gravimetric measurement of water uptake to complement these observations. The observed mass increase of cotton at 70 % RH was 7.1 ± 0.3 % with respect to the dry sample, in agreement with values reported by Cantergiani and Benczédi (2002). Teflon did not exhibit a significant mass change in the same tests.

The desorption phase of the experiments was modeled using a set of differential equations that describe a time-dependent mass balance for nicotine in the gas phase (concentration C in mol. dm^{-3}) and sorbed to i different surface sinks (with a surface concentration of S_i in each of them, expressed in mol. m^{-2}). Its analytical solution provides a general expression for nicotine gas-phase concentration C as a function of time that can be used to fit the experimental data:

$$C(t) = C_0 \exp(-\lambda t) + \sum_i \frac{A}{V} \frac{k_i}{(\lambda - k_i)} S_{i,0} \{\exp(-k_i t) - \exp(-\lambda t)\} \quad (1)$$

where λ is the air exchange rate (in min^{-1}), A and V are the chamber area and volume respectively and k_i is the desorption rate corresponding to the i -th surface sink (in min^{-1}). Equation 1 assumes that adsorption rates to each sink are much slower than air exchange rates. The parameters λ and C_0 can be measured experimentally. We fitted equation 1 (for $i = 1$ and $i = 2$) to the data points shown in Figures 1-A and 1-B employing a least squares method to obtain the best fits for k_i , and for $S_{i,0}' = S_{i,0}(A/V)$, an equivalent initial surface concentration that allows for a direct comparison with C_0 (both in ppb). The adjusted parameters are reported in Table 1, and the fitted curves are shown in Figure 1, together with the experimental values.

Table 1: Parameters fitted to nicotine desorption curves shown in Figure 1.

	Teflon		Cotton	
	Dry air	Wet air	Dry air	Wet air
C_0 / ppb	1491	1460	1592	1610
Single-sink model ($i = 1$)				
S_{0}' / ppb	375	729	10500	10030
k / min^{-1}	3.9×10^{-4}	2.9×10^{-4}	4.8×10^{-4}	5.4×10^{-4}
Dual-sink model ($i = 2$)				
$S_{1,0}'$ / ppb	264	488	5020	5460
$S_{2,0}'$ / ppb	195	244	5580	3010
k_1 / min^{-1}	2.3×10^{-4}	1.8×10^{-4}	2.6×10^{-4}	3.9×10^{-4}
k_2 / min^{-1}	4.5×10^{-3}	3.1×10^{-3}	1.9×10^{-3}	4.8×10^{-3}

Estimated initial surface concentrations $S_{i,0}'$ were 14-28 times higher for cotton relative to Teflon. Yet the desorption rates from those two surfaces were similar. For both systems the presence of water had a marginal effect on the desorption rates. The single-sink model provided a relatively good fit for nicotine desorption from Teflon surfaces and the fit was not significantly improved by addition of another sink. In contrast, the two-sink model was needed to reproduce experimental results with cotton. This suggests two different sorptive states having differing desorption rates for the nicotine-cotton system. Those two surface states are likely related to interactions with two different adsorbent sites, and/or involve different sorbate moieties (such as the pyridinic and the pyrrolidinic amino group in the case of nicotine).

ATR-FTIR Experiments: The chemical nature of the interaction of volatile amines with surface materials was investigated with ATR-FTIR. Figure 2 shows spectra obtained when pure gypsum was deposited on the ATR crystal (A), when pure pyridine was applied on the crystal (B) and when pyridine was adsorbed on the gypsum film as described above (C). In the latter case, the spectral signature corresponding to aromatic C-H stretching (narrow bands between 2950 and 3100 cm^{-1}) was preserved, but an additional broad band was observed at higher energies, in the range 3000-3600 cm^{-1} . That signal can be attributed to N-H and/or O-H stretching resulting from hydrogen-bonding between the amine and an OH group in the substrate surface (Brønsted-type acidic adsorption sites).

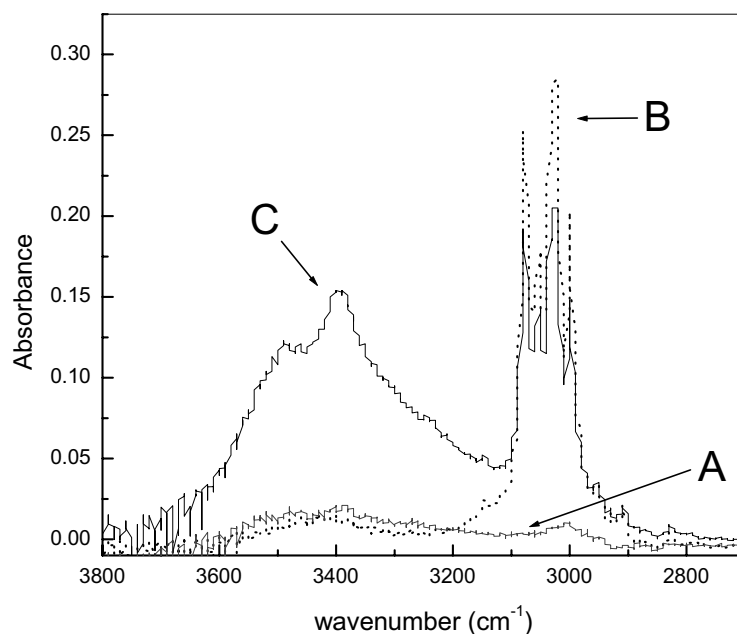


Figure 2: ATR-FTIR spectra of pure gypsum (A), pure pyridine (B) and of pyridine sorbed on gypsum (C).

We analyzed the relative lability of pyridine adsorbed to different surface sites by following the intensity of the two main spectral signatures during desorption of the amine under a nitrogen stream. Figure 3 shows on the left axis the absorbance corresponding to each peak and on the right axis the absorbance ratio NH/CH, as a function of desorption time. Assuming that the C-H signal (at 3025 cm^{-1} for both substrates) was a good indicator for “total pyridine”, the desorption rate corresponding to the hydrogen-bond associated substrate (measured at 3390 and 3500 cm^{-1} for gypsum and at 3340 cm^{-1} for cellulose) was slower than for the physisorbed molecule. This observation is consistent with the presence of two distinct sorptive states, as observed in the chamber studies.

Modeling of indoor sorption and desorption of organic pollutants usually involves the definition of two different surface compartments: a “fast” and a “slow” reservoir or sink, from which chemicals are allowed to desorb at different rates (Piade et al. 1999; Singer et al. 2004). Those two sinks represent a variety of chemical and physical phenomena taking place on material surfaces, comprising not only the chemical diversity of surfaces exposed to indoor air, but also the possible presence of “embedded” or less accessible sinks. Our results show that, even for very simple surfaces, volatile and semivolatile amines may exhibit a desorption behavior involving more than one sink, as a consequence of acid-base and other strong interactions with surfaces.

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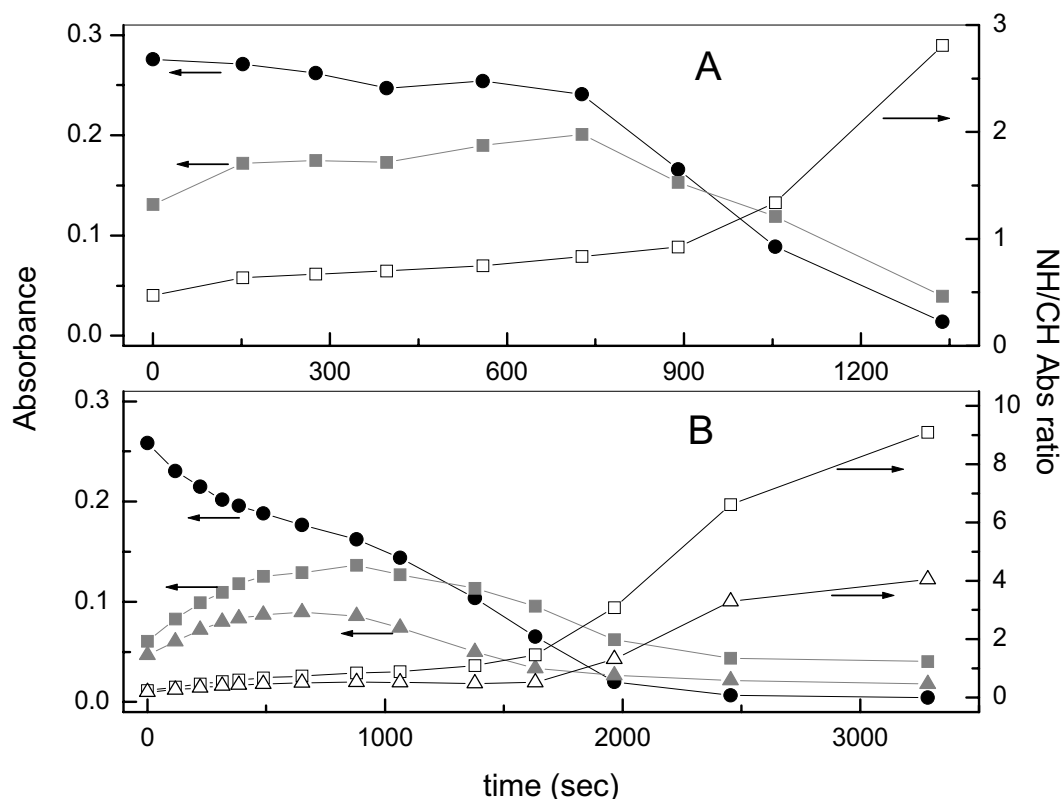


Figure 3: Desorption of pyridine from cellulose (A) and gypsum (B) films. Infrared absorbance (left axis) of C-H bands at 3025 cm^{-1} (●), N-H bands at (A) 3340 cm^{-1} (■); (B) 3390 cm^{-1} (■) and 3500 cm^{-1} (▲). Abs ratios NH/CH (Δ , \square) shown on the right axis.

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